



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> C08F 210/16, 2/34	<b>A1</b>	<b>(11) International Publication Number:</b> WO 94/03509 <b>(43) International Publication Date:</b> 17 February 1994 (17.02.94)
<b>(21) International Application Number:</b> PCT/US93/07358 <b>(22) International Filing Date:</b> 5 August 1993 (05.08.93)  <b>(30) Priority data:</b> 07/926,009                      5 August 1992 (05.08.92)                      US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520 (US). <b>(72) Inventors:</b> HLATKY, Gregory, George ; 1114 Indian Au- tumn, Houston, TX 77062 (US). MONTAGNA, Angelo, Anthony ; 3702 Inwood Drive, Houston, TX 77019 (US). <b>(74) Agents:</b> BELL, Catherine, L.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US) et al.		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> GAS PHASE POLYMERIZATION OF ETHYLENE AND C <sub>7</sub> TO C <sub>10</sub> OLEFINS  <b>(57) Abstract</b>  This invention relates to a method for preparing ethylene-olefin copolymers by gas phase polymerization, especially ethylene-octene copolymer, said copolymers having a density of from about 0.850 to about 0.940 g/cc. Polymerization occurs in the presence of a Group 4,5 or 6 transition metal catalyst system which is activated by an organoaluminum cocatalyst or an ion exchange reagent containing a stable, non-coordinating anion.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

- 1 -

GAS PHASE POLYMERIZATION OF ETHYLENE  
AND C<sub>7</sub> TO C<sub>10</sub> OLEFINS

FIELD OF THE INVENTION

5           This invention relates to a method for preparing ethylene- C<sub>6</sub> to C<sub>10</sub>  $\alpha$ -olefin copolymers by gas phase polymerization in the presence of a transition metal catalyst system which is activated by an organoaluminum cocatalyst or an ion exchange reagent containing a stable non-coordinating anion.

BACKGROUND OF THE INVENTION

10           Copolymers of ethylene and an  $\alpha$ -olefin having 6 to 10 carbon atoms are desired for a variety of applications. The nature, content and distribution of the comonomer in the copolymer significantly influences its physical and chemical properties. Ethylene homopolymers such as high density polyethylene (HDPE) have a density of 0.94 to 0.96 g/cc and are generally linear -- without any  
15           substantial side chain branching --whereas low density polyethylenes (LDPE) have a density of 0.915 to 0.940 g/cc is a highly branched polyethylene, i.e., relatively large numbers of long chain branches extend from the main polymer backbone. In contrast, a linear type of ethylene polymer may be produced having a density in the range of low density polyethylene, or less, by copolymerizing ethylene with an  $\alpha$ -  
20           olefin comonomer -- such as hexene, octene or decene -- to introduce enough short chain branches into the otherwise linear ethylene polymer to reduce its density in an amount which is proportional to that amount of comonomer which is incorporated into the polymer. In a linear copolymer of ethylene density decreases with increasing amounts of incorporated comonomer. A polymer of ethylene  
25           which incorporates an amount of  $\alpha$ -olefin comonomer to provide a density of 0.915 to 0.94 g/cc is referred to as linear low density polyethylene (LLDPE), even higher levels of  $\alpha$ -olefin comonomer incorporation provide a polymer of density ranging from 0.85 to 0.90 g/cc and this material is referred to as very low density polyethylene (VLDPE). For applications such as extrusion coating or blown film,  
30           a low or very low density linear polyethylene is preferred.

          The nature of the comonomer utilized in preparing a linear copolymer of ethylene may exert a significant influence on other properties of the polymer, such as impact strength and gaugeability. For instance, a copolymer prepared with 1-octene as the comonomer has greater impact strength and gaugeability than does  
35           an ethylene copolymer prepared with 1-hexane or 1-butane at a similar level of comonomer incorporation. Further, the manner and randomness with which a

- 2 -

comonomer is distributed throughout the polymer molecules affects other polymer properties such as tear strength, surface properties, cling development, and levels of extractables. Still further, the uniformity of comonomer content between polymer fractions of different molecular weight -- compositional distribution -- affects various properties of the copolymeric material. For instance, linear low density polyethylenes heretofore produced under low or moderate pressures with a conventional Ziegler-Natta type catalyst have a relatively broad molecular weight distribution, i.e.,  $M_w/M_n$  greater than about 3, while also having a relatively broad compositional distribution in that the mole % proportion of  $\alpha$ -olefin comonomer incorporated into molecules of lower molecular weight is greater than the amount incorporated into polymers of higher molecular weight. LLDPE resins of such characteristics are subject to anisotropic properties in the machine versus transverse direction of a fabrication process. The lower molecular weight fraction of such LLDPE resins, in which the copolymer is concentrated, tends to exhibit high block and tackiness and interferes with the proper function of certain additives compounded in the resin and increases the percentage of extractable polymer. The relatively high comonomer content of these low molecular weight polymers molecules causes such polymer molecules to be generally amorphous and migrate to the surface of fabricated parts, thereby producing an undesirable sticky surface.

The randomness with which a comonomer is distributed within a polymer chain -- sequence distribution -- also influences properties of the polymer such as tear strength and film clarity.

Further influencing the properties of a polymer resin is its weight average molecular weight ( $M_w$ ) and molecular weight distribution (MWD). Generally, a greater strength is achieved with a polymer of higher molecular weight and narrower molecular weight distribution. The molecular weight and molecular weight distribution of the polymer affects its rheologic characteristics, modulus and yield strength.

The molecular characteristics of a polymer, particularly a copolymer, in significant part, are dictated by the nature of the catalyst used in its production. For example, a conventional Ziegler-Natta catalyst is a multi-site catalyst, which typically produces a polyolefin of a high molecular weight but of broad molecular weight distribution (MWD; namely,  $M_w/M_n \geq 5$ ). In contrast, an alumoxane-activated metallocene catalyst system is a single-site catalyst which typically produces a polymer of narrow molecular weight distribution (i.e.,  $MWD \leq 3$ ), but at the cost of a typically high content of metallic catalyst residue because of the

- 3 -

high content of alumoxane required to render the metallocene component sufficiently catalytically active for practical use.

Recently a single-site metallocene type of catalyst has been developed which preserves the desirable characteristics of an alumoxane activated metallocene catalyst system while eliminating the need for large amounts of alumoxane to achieve sufficient catalytic activity. The newly developed catalyst system comprises a metallocene component which is activated to a catalytic state by reaction with an ion exchange compound as described in commonly owned copending U.S. Serial numbers 133,052; 133,480; 542,236 and 796,729. These new ionic metallocene catalyst systems are also single-sited catalyst which typically produces polymers of high molecular weight and narrow molecular weight distribution.

In part then, the set of polymers properties may be "engineered" by the choice of the catalyst system selected. For production of a high molecular weight and broad molecular weight distribution polymer, a Ziegler-Natta catalyst may be selected; for production of a high molecular weight and narrow molecular weight distribution polymer, a single-site metallocene type catalyst may be chosen. Further, in part, the properties of a copolymer may be engineered by selecting a particular comonomer. For example, an ethylene/1-octene copolymer provides a polymer of greater impact strength and gaugeability than a copolymer produced with a comonomer of a lesser number of carbon atoms, such as 1-hexene or 1-butene.

Even though it is conceptually possible to engineer the molecular characteristics of a copolymer to a particular set of properties by selection of catalysts and comonomers, the "engineered" polymer must still be practically produceable. That is, with the catalyst, comonomer and the polymerization process conditions selected, the polymer must be producible at a practical rate and cost of polymer production.

Polyolefins, particularly ethylene- $\alpha$ -olefin copolymers have heretofore been produced by a wide variety of processes ranging from solvent, slurry, high temperature-pressure, and gas phase polymerization processes which are carried out over a wide range of temperature and pressure. In a solvent process, polymerization of monomers occurs in the medium of a solvent, typically an inert hydrocarbon, which carries the catalyst into contact with the monomer dissolved therein and the medium is one in which the product polymer is soluble. The solvent medium absorbs the heat generated by the polymerization reaction and heat

- 4 -

exchange control of the solvent medium temperature controls the temperature of the polymerization reaction thereby optimizing productivity or polymer properties according to the characteristics of the catalyst used. After polymer production, the solvent medium and dissolved polymer must be separated by a subsequent processing step, such as by evaporation or distillation.

In slurry processes, monomer polymerization occurs in the medium of a fluid in which the polymer product is insoluble or poorly soluble and, as polymer is produced, it precipitates or beads up in the medium while unreacted monomer remains in fluid form. The temperature of the polymerization reaction is controlled by controlling the temperature of the slurry medium. The slurry medium must be separated from the polymer product by a subsequent processing step. Unreacted monomer is also recovered for recycle in subsequent polymerization reactions.

Any processing step needed after the polymerization reaction to recover polymer product increases its cost of production and, if practically possible, is desirably avoided.

Where possible, polymerization procedures producing polyolefin in particle form are desirable. This consideration makes slurry and gas phase procedures preferred to a solution polymerization procedure where the product polyolefin is produced in dissolved form. Nevertheless, a slurry procedure cannot be used to produce low density ( $\leq 0.93$  g/cc) polymer particles, such as linear low density polyethylene (LLDPE) and very low density polyethylene (VLDPE). While such low density polymers are not soluble in the slurry polymerization fluid, they often become swelled by the fluid medium because of their  $\leq 0.93$  g/cc density. This unwanted swelling produces a gelatinous polymer mass in the reactor rather than discrete polymer particles. Accordingly, such low density polymers are typically produced by a gas phase polymerization procedure. An additional advantage in a gas phase procedure is that no fluid medium is used, hence the need to separate the polymer product from the fluid, or purify the recovered fluid before reuse, is avoided. Further, in gas phase procedures, recovery of unreacted monomer for reuse is also simplified.

Although, for reasons noted, gas phase is a preferred technique for production of LLDPE and other low density types of ethylene polymers, gas phase polymerization is subject to its own inherent difficulties and limitations when producing particulate product. In the gas phase technique, there is no liquid solvent or fluid diluent utilized which can transfer the heat of the polymerization reaction away from the reaction site, i.e., the catalyst surface. Gas phase



- 5 -

polymerization temperature control may be achieved in part by the use of an inert gas, such as nitrogen, and a fluidized bed of small solid polymer particles as a solid diluent, for heat transfer.

5        In gas phase polymerization, polymerization is initiated with an initial bed of polymer granules. Solid supported catalyst particles and monomers are continuously supplied to the reaction zone of the reactor as the bed is fluidized or agitated. The fluidization of the bed insures intimate mixing of the catalyst and monomer as the product polymer is produced in particle form. The temperature of the polymerization reaction is, in significant part, controlled by regulation of the  
10       temperature of the gases fed to the reaction zone. A material balance is maintained in the reactor reaction zone of the reactor by periodic or continuous removal of bed polymer particles to maintain the fluidized bed within constant prescribed weight limits.

15       Critical to the proper operation of a fluidized bed gas phase reaction procedure is the ability to continuously remove polymer particles from the bed to maintain the bed weight within prescribed limits. Hence, production of product polymer as discrete free-flowing particles is essential, since this is essential to their removal from the reaction zone.

20       When localized overheating occurs in a gas phase procedure, the polymer particles which form about the solid supported catalyst particles may melt then solidify upon cooling to produce adherent agglomerations of particles, (i.e., polymer chunks and sheets), which foul the gas phase reactor. This phenomenon is an obstacle to practical use of a gas phase procedure. In commercial practice, gas phase polymerization is conducted in a continuous manner, with a product material  
25       stream (polymer, catalyst, unreacted monomer, etc.) being continuously removed from the reaction vessel at a rate equal to that at which a reagent material stream of monomer and fresh catalyst is supplied to the reaction vessel. Formation of polymer chunks and sheets within the gas phase reaction vessel interferes with and may block the ability to continuously remove a product material stream from the  
30       reactor. This would require shutdown of the reactor for defouling treatment. In an ideal mode of operation shutdown of the gas phase reactor would never be required.

35       To date several methods of copolymer production by a fluidized bed gas phase procedure have been suggested. U.S. Patent 4,469,855 to Cooper notes that condensation of low volatility comonomer in the reaction zone or in the recycle circulation gas loop is a particular problem when attempting to produce a

- 6 -

copolymer of low density. As a solution to this problem, Cooper describes the use of an inert gaseous diluent, such as N<sub>2</sub> or ethane, in the feed gas monomer mixture to permit the maintenance of a comonomer partial pressure which is less than that of its saturated vapor pressure at 60°C while monomer polymerization is  
5 conducted over a Ziegler-Natta type catalyst at a polymerization temperature of at least 60°C but less than 110°C. Under such constraints the quantity of comonomer which can be incorporated into the polymer is limited to an amount no greater than about 0.5 mole%, and the copolymer has a relatively broad MWD and a density in the LLDPE range.

10 U.S. Patent 4,522,987 to Hogan et al. describes a gas phase procedure using a specific catalyst composition whereby comonomer is more efficiently incorporated into the copolymer product, thus allowing lower concentrations of comonomer to be used which in turn permits the monomer feed stream to be of lower entry temperature (i.e., 25-60°C) so the monomer feed stream may be used  
15 to control polymerization temperature to a range of between 70-120°C. Again, a copolymer produced by this process would be of relatively broad MWD and have a density like that of LLDPE.

United Kingdom Patent Application for Cozewith describes gas phase polymerization with vanadium catalysts for the production of elastomeric  
20 copolymers of ethylene and  $\alpha$ -olefins up to C<sub>10</sub>, but C<sub>3</sub> to C<sub>5</sub> are preferred because of practical limitations of temperature and pressure in gas phase. Likewise, U.S. Patent 5,106,804 to Bailey produces ethylene-butene copolymers in gas phase using zirconium metallocenes with alumoxane activators. U.S. Patent 5,100,979 to Eisinger, et al. discloses the gas phase polymerization of ethylene and  
25 octene in gas phase fluidized bed reactor with a Vanadium catalyst and a hydrocarbyl aluminum co-catalyst, however the volume of octene that must be used with the vanadium catalyst to obtain the small amount of incorporated monomer is too large for practical purposes.

Despite the suggestions of Cooper, Hogan et al., Cozewith, Bailey and  
30 Eisinger to date and so far as is known, a gas phase procedure has not been commercially used for production of a copolymer of ethylene and a comonomer with 6 or more carbons.

Copolymers of ethylene with comonomers having six or more carbon atoms have various advantageous properties, such as improved impact strength and  
35 gaugeability among others, compared to analogues produced with a comonomer of lower carbon number. A method for their practical production by a gas phase



- 7 -

polymerization procedure which would allow one to enjoy the advantages inherent in gas phase processing has yet to be realized.

### SUMMARY OF THE INVENTION

5 This invention relates to the discovery that discrete olefin polymerization catalyst systems containing Group 4, 5 or 6 transition metals are capable of polymerizing ethylene with one or more olefin comonomers, preferably having six to ten carbon atoms, more preferably seven to ten carbon atoms, even more preferably eight to ten carbon atoms under gas phase reaction conditions with a high rate of incorporation of the comonomer into the copolymer product.

10 Preferable catalyst systems comprise activated cyclopentadienyl transition metal catalyst systems. The activating agent may be an alumoxane or a non-coordination anion. For a given concentration of a comonomer in the reaction zone a greater amount of comonomer is incorporated into a narrow molecular weight distribution copolymer product with the activated cyclopentadienyl catalyst than has heretofore

15 been possible to incorporate under gas phase conditions with use of other types of catalysts.

The process comprises contacting, in a reaction zone, ethylene and one or more olefin comonomers with an activated cyclopentadienyl transition metal catalyst composition, under conditions of temperature and pressure which maintain

20 the ethylene-comonomer mixture in a gaseous state to produce an ethylene- $\alpha$ -olefin copolymer having a density of from about 0.850 to about 0.940 g/cc.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention in its preferred embodiments relates to a gas phase process for polymerizing ethylene in combination with olefin monomers such as  $\alpha$ -olefins and di-olefins, including mono-enes, di-enes, and poly-enes, in the presence of an

25 activated cyclopentadienyl transition metal catalyst which comprises the reaction product of a transition metal compound and an ionic exchange composition or alumoxane.

The polymerization is typically accomplished at a temperature below the

30 temperature at which particles of polymer product may fuse while the concentration of comonomer is maintained below its dew point for the temperature and pressure conditions maintained in the reaction zone. Since the activated catalysts of this invention incorporate monomer into the growing copolymer chain in higher amounts, i.e. have a higher reactivity ratio, smaller volumes of the C6 to

35 C10 olefin comonomer are necessary to make the desired polymer. Thus copolymers with high comonomer content are a preferred product of this

- 8 -

invention. Likewise this invention also provides a method for obtaining ethylene copolymers that is more efficient at incorporating the desired amount of monomer. Copolymers having a high comonomer content relative to the concentration of comonomer and molar ratio of ethylene to comonomer in the reaction zone are also preferred products of this invention.

Comonomer content of a copolymer can be controlled through the selection of the transition metal compound component of the catalyst system and by controlling the partial pressure of the various monomers. The partial pressure of the comonomer in the reaction zone may be maintained up to an amount which would, at a temperature of 10°C less than the temperature of the monomer mixture in the reaction zone, be the saturated vapor pressure of the comonomer to prevent condensation of the comonomer. Likewise the partial pressure of ethylene may be higher than those previously available. In a preferred embodiment ethylene is present in the reaction zone at a partial pressure of greater than about 40 psi (about 275 kPa) ( 1 psi = 6.895 kPa), preferably about 100 (about 689 kPa) to about 250 psi (about 1723 kPa). The partial pressure of the C6 to C10 comonomer is preferably up to about 5 psi (about 34 kPa), even more preferably about 2 to 5 about psi (about 13 kPa to about 34 kPa).

In previously known gas phase polymerization techniques, comonomer present at the high amounts needed to produce polymer with a density of about 0.91 or less would have caused the bed to become liquid. This disadvantage is avoided in the instant invention because the catalyst has such a high reactivity ratio for the comonomers that the comonomer is copolymerized before it can condense into a liquid. Furthermore, the ratio of the ethylene molar concentration to the octene molar concentration is a useful means for controlling the polymerization and the final product properties. In a preferred embodiment, the ratio of the ethylene molar concentration to the octene molar concentration is preferably about up to about 0.05, preferably about 0.02 or less, even more preferably about 0.01 to about 0.02.

The dew point limit has particular limits with higher molecular weight comonomers such as octene. The closer the dew point, the incipient temperature at which a gas begins to condensate into a liquid, the higher the probability that the polymer particles in the fluidized bed will begin to stick together and cause fluidization instabilities. In the preferred embodiment the fluidized bed reactor is operated at a temperature such that the reactor recycle gas has a dew point at least 5 °F below that of the reactor bed, more preferably at least 10°F below the reactor

- 9 -

bed temperature. The octene partial pressure in and of itself is not critical as long as the dew point constraint is not reached. The octene partial pressure contributes to the overall dew point, but its dew point is not a limiting factor. Rather it is the total reaction gas dew point which is a controlling factor. There is no limit on the octene partial pressure except as dictated by the dew point constraint. In general, the limits become more restrictive with higher comonomer molecular weights.

The polymerizations are preferably run at temperatures greater than the dew point of the pure monomers. Thus in a preferred embodiment polymerization is run at a temperature of 120°F or above (about 48°C or above), preferably about 130°F to about 200°F (about 54°C to about 94°C), even more preferably about 160°F to about 180°F (about 71 °C to about 83°C).

A narrow molecular weight distribution ( $M_w/M_n \leq 4$ , preferably  $\leq 3$ ), as measured by Gel Permeation Chromatography using polyethylene standards, is produced having a comonomer content of from about 2 to about 3 times greater than was heretofore possible to produce under gas phase conditions. In a preferred embodiment copolymers having about 10 mole % comonomer or less, preferably having about 4 to about 10 mole% comonomer, are produced. Particularly preferred polymers having 1,000,000  $M_w$  or above with MWD's of 4 or less are produced using bis(cyclo-pentadienyl)hafnium dimethyl and the tri-substituted ammonium salt of tetra(pentafluorophenyl)boron in the absence of a chain transfer agent.

Preferred monomers include linear cyclic or branched olefins having from six to ten carbon atoms, preferably  $\alpha$ -olefins or diolefins having six to ten carbon atoms. Preferred examples of comonomers include, but are not limited to, 1,9-decadiene, hexene-1, octene-1, 4-methylpentene-1, decene-1, norbornene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,7-octadiene, ethylidene norbornene, norbornadiene 3,5,5-trimethyl-hexene-1 and the like.

These comonomers are contacted with ethylene and a catalyst system comprising a transition metal compound having a hydrolyzable ligand activated by either an organoaluminum reagent such as methylalumoxane or an ionic exchange activator composition as described in copending U.S. Patent Application Serial Nos. 133,052; 133,480; 542,236, 796,729 and 810,551, which are incorporated by reference.

#### Activated Catalyst System - General Description

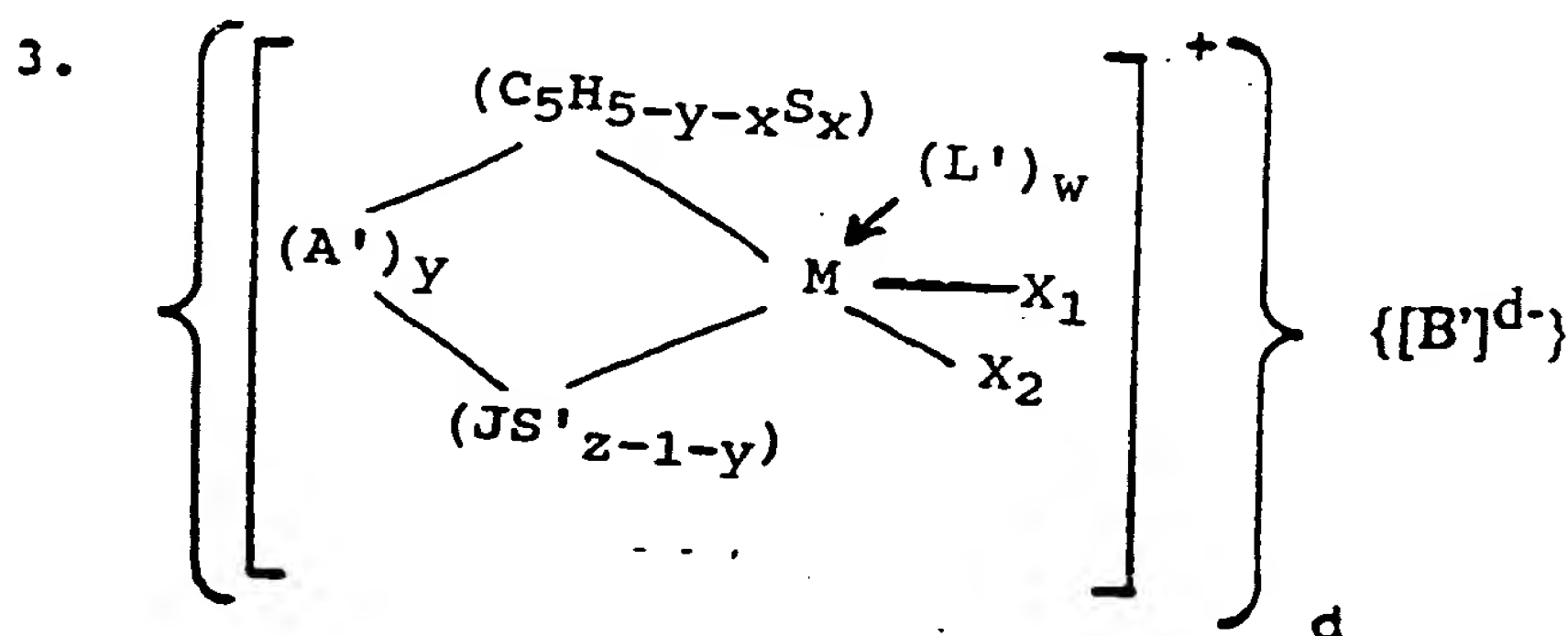
In general, any ligand stabilized hydrolyzable mono, di- or poly-alkyl or hydride complex of a transition metal may be converted into a reactive

- 10 -

coordinatively unsaturated alkyl or hydride cationic complex by reaction with an activator composition as described hereafter. The cationic transition metal complex is catalytically active for polymerization of ethylenically unsaturated monomers. Preferably the catalyst is prepared in heterogeneous, supported form by placement of the catalyst system on a support as described in related, copending U.S. Patent Application Serial No. 810,551 and its continuation in part application, both incorporated by reference in their entirety, or by preparation of the catalyst system in particle form.

Preferred catalysts for use in this invention are formed from a transition metal compound containing at least one ligand which will react with the cation portion of the ionic complex activator. Preferably the ligand is in the nature of a cyclopentadienyl group, as such or as forming part of a polycyclic ligand group. however, any ancillary ligand containing at least one reactive metal-sigma bond can be employed. The preferred ionic catalyst can be represented by one of the following general formulae (all references to Groups being the new group notation of the Periodic Table of the Elements as described by Chemical and Engineering News, 63(5), 27, 1985):

1.  $\{[(A-Cp)MX_1]^{-} \{d\} [B']^d-\}$
2.  $\{[(A-Cp)MX_1L']^{-} \{d\} [B']^d-\}$



wherein:

(A-Cp) is either (Cp) (Cp\*) or Cp-A'-Cp\*; Cp and Cp\* are the same or different cyclopentadienyl ring substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted

**SUBSTITUTE SHEET**

- 11 -

chalcogen or halogen radicals. or Cp and Cp\* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C4 to C20 ring to form a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp\* rings or (C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) and (JS'<sub>z-1-y</sub>) groups;

(C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) is a cyclopentadienyl ring substituted with from zero to five S radicals:

x is from 1 to 5 denoting the degree of substitution;

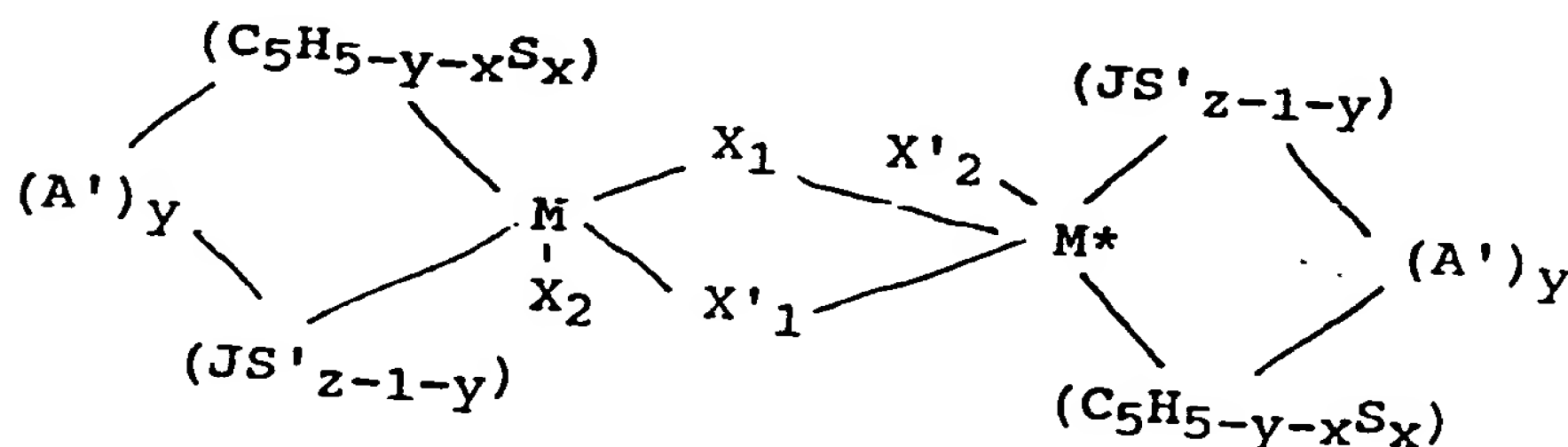
M is Group 4, 5 or 6 metal;

X<sub>1</sub> is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical, which radical may optionally be covalently bonded to both or either M and L' or all or any M, S or S';

(JS'<sub>z-1-y</sub>) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

L' is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M\* are bridged by X<sub>1</sub> and X'<sub>1</sub>, wherein M\* has the same meaning as M and X'<sub>1</sub> had the same meaning as X<sub>1</sub> where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula.



**SUBSTITUTE SHEET**

- 12 -

w is an integer from 0 to 3.

B' is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms; and

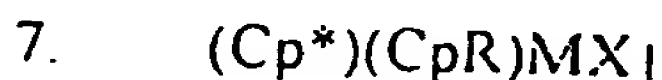
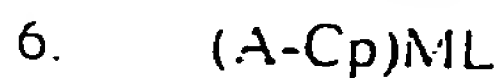
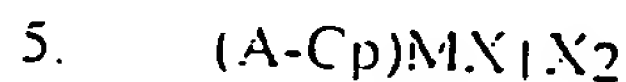
d is an integer representing the charge of B'.

5 The ionic catalysts are prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4, 5 or 6 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atoms or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallocarboranes.

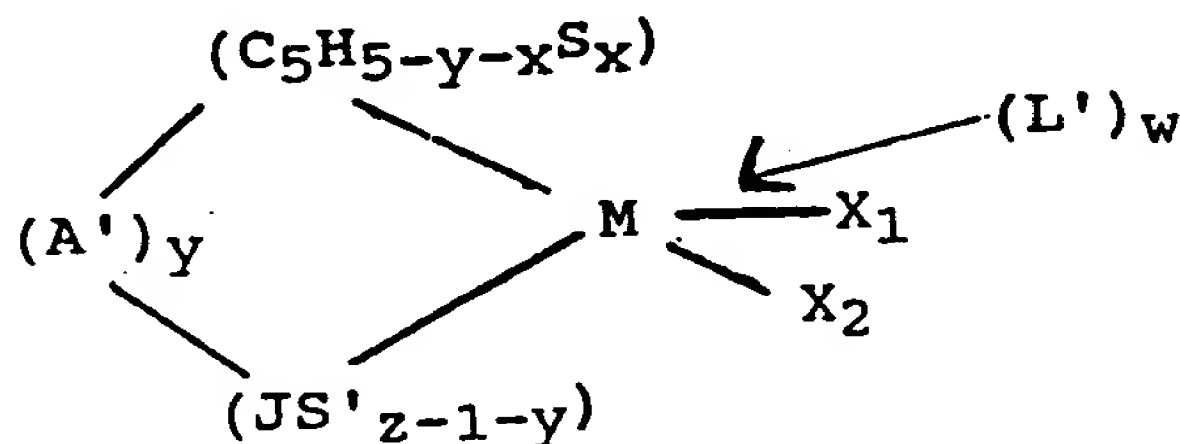
The cation portion of the second component may comprise Bronsted acids such as hydrogen or protonated Lewis bases or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbonium or silver cations.

#### A. Transition Metal Component

20 The transition metal compounds preferred for use as first compounds in the preparation of the ionic catalyst are Pi bonded moieties such as cyclopentadienyl derivatives of group 4, 5 or 6 transition metal compounds, preferably titanium, zirconium and hafnium, represented by the following general formulae:



8.



wherein:

(A-Cp) is either (Cp) (Cp\*) or Cp-A'-Cp\*. Cp and Cp\* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-

**SUBSTITUTE SHEET**



- 13 -

halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radical, or Cp and Cp\* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C<sub>4</sub> to C<sub>20</sub> ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp\* rings or (C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) and JS'(z-1-y) groups;

M is as defined above;

y is 0 or 1;

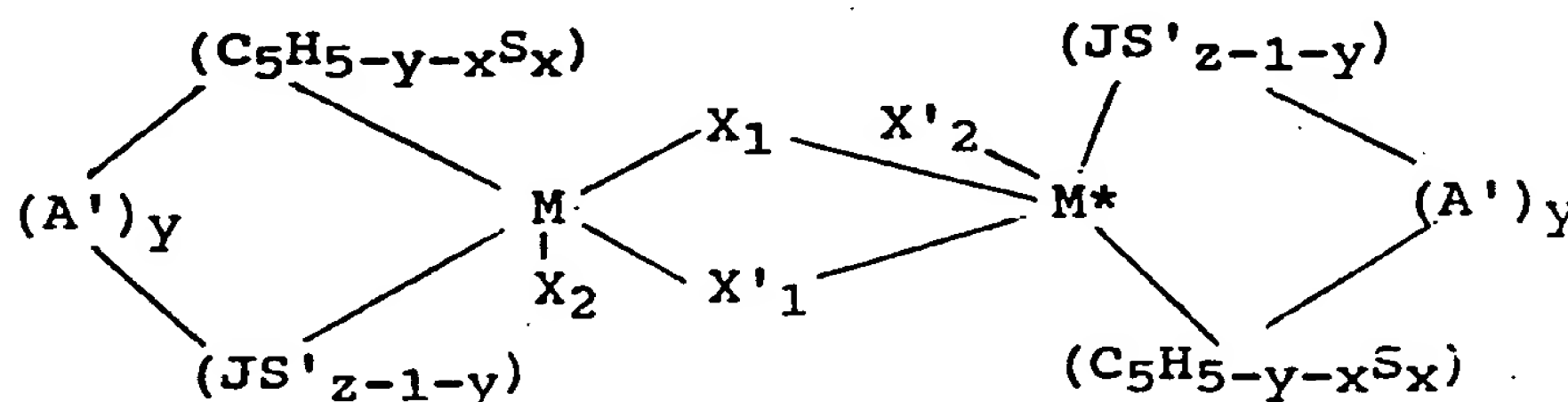
(C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

(JS'z-1-y) is a heteroatom in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

L' is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M\* are bridged by X<sub>1</sub> and X'<sub>1</sub>, wherein M\* has the same meaning as M and X'<sub>1</sub> had the same meaning as X<sub>1</sub> where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:

9.



w is an integer from 0 to 3, and

**SUBSTITUTE SHEET**

- 14 -

X<sub>1</sub> and X<sub>2</sub> are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals; or X<sub>1</sub> and X<sub>2</sub> are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or X<sub>1</sub> and X<sub>2</sub> together can be an olefin, diolefin or aryne ligand.

Table 1 depicts representative constituent moieties for the metallocene components of formulae 6-9. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. Illustrative compounds of the formula 6 type are:

bis(cyclopentadienyl)hafnium dimethyl,  
bis(tetrahydroindenyl)zirconium dihydride,  
bis(pentamethyl)zirconium ethylidene,  
dimethylsilyl(1-fluorenyl)(cyclopentadienyl)titanium dimethyl and the like.

Illustrative compounds of the formula 7 type are:

bis(cyclopentadienyl)(1,3-butadiene)zirconium,  
bis(cyclopentadienyl)(2,3-dimethyl-1,3-butadiene) zirconium,  
bis(penta-methylcyclopentadienyl)(benzyne) zirconium,  
bis(pentamethylcyclopentadienyl) titanium ethylene and the like.

Illustrative compounds of the formula 8 type are: (pentamethylcyclopentadienyl)

(tetramethylcyclopentadienyl-methylene)zirconium hydride,

(pentamethylcyclopentadienyl) (tetramethylcyclopentadienyl-methylene)hafnium benzyl,

(pentamethylcyclo-pentadienyl)(tetramethylcyclopenta-dienylmethylene) zirconium phenyl and the like.

Illustrative compounds of the formula 9 type are:

dimethylsilyl(tetramethyl-cyclopentadienyl) (t-butylamido)zirconium dimethyl,

(methylcyclopentadienyl)(phenylamido) titanium dimethyl,

methylphenylsilyl(indenyl) (phenylphosphido) hafnium dihydride,

(pentamethylcyclopentadienyl) (di-t-butylamido) hafnium dimethyl and the like.

#### B. The Activator Component

Preferred activated catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which upon reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as ([B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(X)]<sup>-</sup>), which stabilizes the cationic transition metal species

- 15 -

which is generated by the reaction. Ionic catalysts can be, and preferably are, prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst system used in the process of this invention comprise a cation, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4, 5 or 6 transition metal cation) which is formed when the two compounds are combined and said anion is sufficiently labile to be displaced by olefinic, diolefinic, and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Three classes of compatible non-coordinating anion compositions have been disclosed in copending U.S. Patent Application Nos. 133,052; 133,480 and 796,729 (herein incorporated by reference): 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core; 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes and boranes; and 3) polyanionic compositions wherein a plurality of either of the above two types of non-coordinating anions are covalently bonded to an atomic, molecular or polymeric complex or particle (T) which forms the central core of the polyanionic composition.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following general formula:



wherein:

H is a hydrogen atom;

[L''-H] is a Bronsted acid;

M' is a metal or metalloid;

Q<sub>1</sub> to Q<sub>n</sub> are, independently hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any one, but not more than one, of Q<sub>1</sub> to Q<sub>n</sub> may be halide radicals;

m is an integer representing the formal valence charge of M'; and

n is the total number of Q ligands.

As indicated above, any metal or metalloid capable of forming an anionic complex which is stable in water may be used or contained in the anion of the

- 16 -

second compound. Suitable metals then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron may be represented by the following general formula:



wherein:

[L''-H] is as defined above;

B is boron in a valence state of 3;

Ar<sub>1</sub> and Ar<sub>2</sub> are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

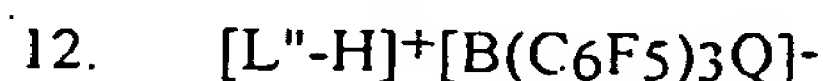
X<sub>3</sub> and X<sub>4</sub> are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals, with the proviso that X<sub>3</sub> and X<sub>4</sub> will not be halide at the same time.

In general, Ar<sub>1</sub> and Ar<sub>2</sub> may, independently, be any aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to, hydrocarbyl radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organo metalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X<sub>3</sub> and X<sub>4</sub>. The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X<sub>3</sub> and X<sub>4</sub> are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as the Ar<sub>1</sub> and Ar<sub>2</sub>, or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X<sub>3</sub> and X<sub>4</sub> may also, independently be

- 17 -

alkoxy of dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and organometalloid radicals and the like. As indicated above, Ar<sub>1</sub> and Ar<sub>2</sub> could be linked to either X<sub>3</sub> or X<sub>4</sub>. Finally, X<sub>3</sub> and X<sub>4</sub> may also be linked to each other through a suitable bridging group.

5 The most preferred activator compounds comprising boron may be represented by the following general formula:

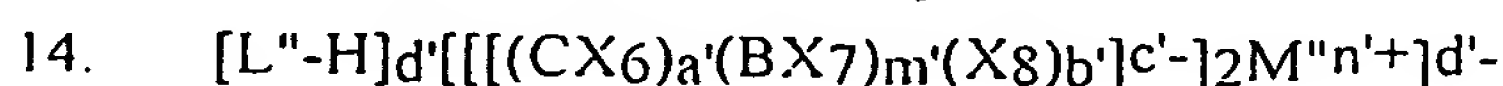


wherein:

F is fluorine, C is carbon and [L''-H], B, and Q are defined above.

10 Illustrative, but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts, e.g., L'' = N,N-dialkylaniline, where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most  
15 preferred anion offer the advantage of providing a solid phase catalyst system which may be used as such in gas phase processing without the need for a separate catalyst support material.

Activator components based on anions which contain a plurality of boron  
20 atoms may be represented by the following general formulae:



wherein:

[L''-H] is either H<sup>+</sup> or a Bronsted acid derived from the protonation  
25 of a neutral Lewis base;

X, X', X'', X<sub>6</sub>, X<sub>7</sub> and X<sub>8</sub> are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl or halocarbyl-substituted organometalloid radicals;

30 M'' is a transition metal;

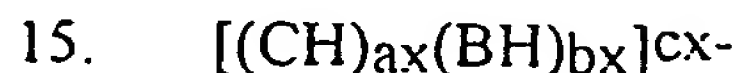
a and b are integers  $\geq 0$ ; c is an integer  $\geq 1$ ; a + b + c = an even numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

a' and b' are the same or a different integer; c' is an integer  $\geq 2$ ; a' +  
35 b' + c' = an even-numbered integer from 4 to about 8; m' is an integer from 6 to about 12; n' is an integer such that 2c' = n' = d'; and d' is an integer  $\geq 1$ .

- 18 -

Preferred anions comprising a plurality of boron atoms are:

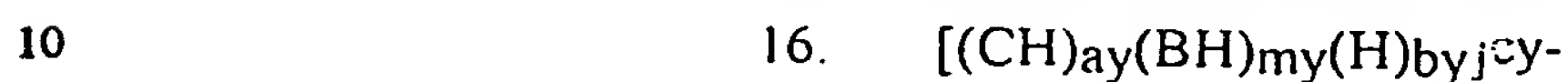
(1) A trisubstituted ammonium salt of a bornane or carborane anion satisfying the general formula:



5            wherein;

ax is either 0 or 1; cx is either 1 or 2; ax + x = 2; and bx is an integer ranging from about 10 to 12;

(2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formulae:



wherein:

ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3; ay + by + cy = 4; and my is an integer from about 9 to about 18; or

15            (3) A trisubstituted ammonium salt of a metallaborane of metallocarborane anion satisfying the following general formula:

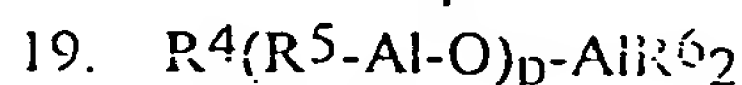
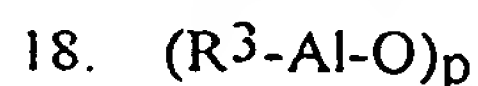


wherein:

20            az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11; az + bz + cz = 4; and nz and dz are, respectively, 2 and 2 or 3 and 1; M<sup>n</sup> is as defined above.

25            The activator composition most preferred for forming the ionic catalyst used in this process are those containing a tetrapentafluorophenyl boron anion or two or more tripentafluorophenyl boron anion groups covalently bound to a central atomic, molecular or polymeric complex or particle. Other examples of activator specific compositions which may be used to form an anionic catalyst useful in this invention are identified and more fully described in European Patent applications 0 277 003 and 0 277 004 which are hereby incorporated by reference.

30            The catalyst used above may also be activated with alumoxanes. Preferred alumoxanes are those alumoxanes represented by the following general formulae:



35            An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are, independently a C<sub>1</sub>-C<sub>6</sub>



- 19 -

alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "p" is an integer from 1 to about 50. Most preferably, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are, each methyl and "p" is a least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more R<sup>3-6</sup> groups may be halide. M' and M are as  
5 described previously and Q' is a partially or fully fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield  
10 an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

The Alumoxane activated transition metal compounds of this invention may be placed on a support as disclosed in U.S. patent 4,808,561 which is herein  
15 incorporated by reference as if fully set forth.

#### C. The Catalyst Support

Typically, the support can be any of the known solid catalyst supports, particularly porous supports, such as talc, silica, inorganic oxides, and resinous support materials such as polyolefins. Preferably, the support material is silica or  
20 an inorganic oxide in finely divided form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2, 4, 13 or 14 metal oxides. The most preferred catalyst support materials include silica, alumina, and silica-alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or  
25 in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like. A preferred support is magnesium chloride as disclosed in US Patent 5,106,804 to Bailey, which is incorporated by reference herein. Other suitable support materials, however, can be employed, for example, finely divided polyolefins such as finely divided polyethylene.

The metal oxide support used in the preparation of the catalyst may be any  
30 particulate oxide or mixed oxide such that it is substantially free of adsorbed moisture. Generally, the metal oxides contain acidic surface hydroxyl groups which may react with and deactivate the ionic metallocene catalyst when the catalyst is added to the slurried metal oxide support. Therefore, if a catalyst support material which contains surface hydroxyl groups is employed, it is  
35 preferred that the support be treated prior to use, e.g., subjected to a thermal or

- 20 -

chemical treatment, in order to remove water and reduce the concentration of the surface hydroxyl groups. The treatment may be carried out in vacuum or while purging with a dry inert gas such as nitrogen at a temperature of about 100°C to about 1000°C, and preferably, from about 300°C to about 800°C. The duration of the thermal treatment can be from about 1 to about 24 hours. Shorter or longer times can be employed provided equilibrium is established with the surface hydroxyl groups.

As an alternative method of dehydration of the metal oxide support material, chemical dehydration can be advantageously employed. Chemical dehydration converts all water and hydroxyl groups on the oxide surface to inert species. Useful chemical agents are for example, chlorosilanes, such as trimethylchlorosilane, dimethylaminotrimethylsilane and the like. The chemical dehydration is accomplished by slurring the inorganic particulate material, such as, for example, silica in an inert low boiling hydrocarbon, such as, for example, hexane. During the chemical dehydration reaction, the silica should be maintained in a moisture and oxygen-free atmosphere. To the silica slurry is then added a low boiling inert hydrocarbon solution of the chemical dehydrating agent, such as, for example, dichlorodimethylsilane. The solution is added slowly to the slurry. The temperature ranges during chemical dehydration reaction can be from about 25°C to about 120°C, however, higher and lower temperatures can be employed. Preferably, the temperature will be about 50°C to about 70°C. The chemical dehydration procedure should be allowed to proceed until cessation of gas evolution. Generally at this point all the moisture is removed from the particulate support material. Normally, the chemical dehydration reaction will be allowed to proceed from about 30 minutes to about 16 hours, preferably 1 to 5 hours. Upon completion of the chemical dehydration, the solid particulate material is filtered under a nitrogen atmosphere and washed one or more times with a dry, oxygen-free inert hydrocarbon solvent. The wash solvents, as well as the diluents employed to form the slurry and the solution of chemical dehydrating agent, can be any suitable inert hydrocarbon. Illustrative of such hydrocarbons are heptane, hexane, toluene, isopentane and the like.

Once treatment to minimize or reduce, the surface hydroxyl groups is complete, it is preferred to further treat the support media with an aluminum alkyl solution, preferably about 3 mmol of 1M hexane solution per gram of support isolated. This treatment generally leads to an increase in catalytic activity and prolonged shelf life of the supported catalyst system. It has been found that when

- 21 -

employing the supported ionic catalyst of the subject invention in conjunction with an organoadditive, such as a Group 13 additive, during polymerization, increased catalytic efficiency and reduced reactor fouling is observed. If a support media is employed where dehydration to remove surface hydroxyl groups is not necessary, one may optionally proceed to treat the support with the aluminum alkyl to obtain the benefits disclosed. A further optional step to employ is to prepolymerize the supported catalyst system with an olefinic monomer in order to strengthen particle size of the polymer product formed.

The specific particle size, surface area, pore volume, and number of surface hydroxyl groups characteristic of the inorganic oxide determine the amount of inorganic oxide that it is desirable to employ in preparing the catalyst compositions, as well as affecting the properties of polymers formed with the aid of the catalyst compositions, these characteristics must frequently be taken into consideration in choosing an oxide for use in a particular aspect of the invention. For example, since the catalyst composition is to be used in a gas-phase polymerization process - a type of process in which it is known that the polymer particle size can be varied by varying the particle size of the support - the inorganic oxide used in preparing the catalyst composition should be one having a particle size that is suitable for the production of a polymer having the desired particle size. In general, optimum results are usually obtained by the use of inorganic oxides having an average particle size in the range of about 30 to 600 microns, preferably about 30 to 100 microns; a surface area of about 50 to 1,000 square meters per gram, preferably about 100 to 400 square meters per gram; and a pore volume of about 0.5 to 3.5 cc per gram; preferably about 0.5 to 2 cc per gram.

#### D. Catalyst Preparation and Use

The supported ionic metallocene catalyst used in this invention may be prepared by combining the metallocene component, the activator component and the support. Typically this combination occurs in a suitable solvent in one or more steps. It is preferred that the metallocene and activator components be combined in the presence of a suitable solvent or diluent as a first step and thereafter the metallocene-activator product be contacted with the support. Suitable solvents include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, isohexane, heptane, octane and the like; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like; and aromatic

- 22 -

and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. The aromatic and alkyl-substituted aromatic solvents are preferred.

While the supported ionic metallocene catalysts do not contain pyrophoric species, it is nevertheless preferred that the catalyst components be handled in an inert, moisture-free, oxygen-free environment such as argon, nitrogen or helium because of the sensitivity of the catalyst components to moisture and oxygen.

In a preferred method, the metallocene and activator components are combined in a first step in an aromatic solvent to produce a catalytic solution. This reaction may be carried out in the temperature range of from  $-100^{\circ}$  to about  $300^{\circ}$  C, preferably about  $0^{\circ}$  to about  $100^{\circ}$  C. Holding times to allow for the completion of the reaction may range from about 10 seconds to about 60 minutes depending upon variables such as reaction temperature and choice of reactants.

The catalytic solution produced by combining the metallocene and activator components is then contacted with the support. The method of contact may vary, but it is preferred that the catalytic solution be added to a rapidly stirred slurry of the catalyst support in a hydrocarbon solvent, preferably an aliphatic solvent. Contact temperatures may range from about  $0^{\circ}$  to about  $100^{\circ}$  C depending upon the solvents used. Contact times may vary from about 10 seconds to about 60 minutes, longer contact times than 60 minutes not providing any significant additional benefits. In a preferred embodiment the activated catalyst is placed in slurry of the dried support material in an aliphatic solvent for a contacting period of from about 10 seconds to about 60 minutes.

The activated catalyst is contacted with an alumina, silica or silica-alumina support to produce the most preferred activated catalyst.

In the preparation of the supported catalyst, the reagents should be combined to provide a catalyst concentration (metallocene and activator) on the support of from about 0.01 wt.% to about 20 wt.%, preferably about 1 wt.% to about 5 wt.% based upon the weight of the support.

An alternative embodiment of this invention is to place the activator component on a support employing the steps disclosed above. The supported activator may be stored as is, under inert conditions, to be combined at a later time with a metallocene component. A further alternative is to place the metallocene component on a support and store as is, to be later activated by an activator component. In another preferred embodiment of the invention the activated catalyst is placed on a support according to the method disclosed in copending United States Application Number USSN 7/885,170 filed 5-18-92.

- 23 -

In a most preferred embodiment of the present invention, the catalyst system is formed with a bis(cyclopentadienyl) titanium or zirconium compound, like those of formulae number 5-7. Examples of preferred compounds and activators include but are not limited to bis(cyclopentadienyl)zirconium dimethyl or  
5 bis(cyclopentadienyl)hafnium dimethyl reacted with N,N-dimethylanilinium tetra(pentafluorophenyl)boron (DMAH) or methylalumoxane.

Employing a mixed metallocene catalyst system can achieve molecular weight distributions within the range of about 1.5 to about 15. The substituents of the cyclopentadienyl radicals, however, can exert a profound influence on polymer  
10 molecular weights and degree of comonomer incorporation.

A particularly surprising feature of some of the supported catalysts of this invention, particularly those based on hafnocenes in combination with an activator component comprising perfluorinated tetraphenylborate anions, is that when the catalysts of this invention are used to copolymerize ethylene and  $\alpha$ -olefins alone or  
15 in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts, vanadium catalysts and bis(cyclopentadienyl)zirconium catalysts. The relative rates of reaction of ethylene and higher  $\alpha$ -olefins with the aforementioned hafnium-  
20 based catalysts are much closer than with conventional Ziegler-Natta type catalysts of the Group 4 metals. The comonomer distribution in copolymers prepared with the catalysts will range from about near perfectly alternating to statistically random. Consequently, the hafnocene based ionic metallocene supported catalysts are particularly preferred.

In other embodiments of the invention wherein the catalyst system is formed with a cyclopentadienyl transition metal compound like that of formula number 8, titanium is the preferred transition metal. In this case a titanium species of the catalyst generally exhibit higher catalyst activities and permit production of polymers of greater molecular weight and greater amounts of incorporated  
30 comonomer than do analogous species of zirconium or hafnium.

#### **The Polymerization Process**

The polymerization of ethylene and comonomer is effected using an activated catalyst system as described, preferably the catalyst is supported as described. The polymerization is carried out in a continuous gas phase, preferably  
35 in a fluidized bed reactor. Polymerization is initiated with an initial bed of polymer granules, preferably the polymer of the initial bed is of like kind to the copolymer



- 24 -

to be produced as product polymer. Solid supported catalyst particles and monomers are continuously supplied to the reaction zone of the gas phase reactor while the bed is fluidized or agitated. Preferably the gas mixture comprising the monomers is utilized to fluidize the bed. As the polymerization reaction proceeds  
5 a material balance is maintained in the gas phase reaction zone by periodic or continuous removal of bed particles to maintain the bed within prescribed desired limits. In general it is desirable to keep the bed level at its maximum height to maintain a high production rate.

Temperature control is effected by control of the temperature of gas  
10 mixture feed to the reaction zone, the concentration of monomers within the gas mixture feed to the reaction zone, the concentration of catalyst feed to the reaction zone, or by evaporation of a hydrocarbon spray supplied to the reaction zone, or by a combination of two or more of these means for control. Preferably the temperature of the reaction zone is controlled to be between about 130 to 190°F  
15 (54 to 88°C) to minimize the chance of reactor fouling by fusion of polymer particles within the reaction bed or along the walls of the reaction zone.

Bed temperature is preferably controlled by a combined control of inlet feed gas mixture temperature, recirculating gas temperature and concentration of catalyst supplied to the reaction zone. Generally, it is preferred to supply the feed  
20 gas to the reaction zone at a temperature in the range of from about 0 to about 50° C and to supply a monomer concentration and catalyst concentration to the zone sufficient to produce a heat of reaction from the polymerization reaction that will maintain a gas temperature in the zone which is 5 to 50°C higher than the temperature of the feed gas.

25 The feed gas supplied to the reaction zone in part comprises ethylene, the balance being the selected olefin comonomers alone or a combination of comonomer with an inert diluent gas such as nitrogen or ethane. When a diluent gas is used, it is preferably nitrogen. To prevent condensation of comonomer within the reaction zone to a liquid phase that could disrupt fluidization of the bed,  
30 the concentration within the feed gas must be limited to be below that amount which, at the condition of pressure and reaction gas temperature maintained within the zone, causes the comonomer to exceed its saturated vapor pressure. Thus the partial pressure of the comonomer must be carefully observed and controlled. For the condition of pressure existing in the reaction zone, the amount of comonomer  
35 supplied thereto should provide a partial pressure of the comonomer which is less than the saturated vapor pressure of the comonomer at that temperature which is



- 25 -

less than the reaction zone temperature, and preferably 5°C less than the reaction zone temperature. In a preferred embodiment a polymerization temperature of about 80°C plus or minus ten degrees C will be maintained in the reaction zone and the inlet gas will be maintained at or below a partial pressure equal to the saturated vapor pressure of the comonomer feed at the reactor temperature. The inlet gas is preferably 5°C or more below the reactor temperature, more preferably 10°C or more below the reactor temperature.

With respect to the amount of comonomer supplied to the reaction zone, the amount of ethylene supplied may then be selected to provide a copolymer product having the desired mole% of incorporated comonomer -- which is dependent upon the particulars of the ionic catalyst system used. Accordingly, under some conditions of gas phase operation, depending upon the desired content of comonomer to be incorporated into the copolymer product, the feed gas may be ethylene and comonomer alone. Under other conditions it may be necessary to use an inert diluent gas as a component in the feed gas either to produce a copolymer of the desired comonomer content or to aid in temperature control in the reaction zone or both. In any event, by reason of the catalyst system with which the gas phase reaction is carried out, it is possible to minimize the amount of diluent gas which may be needed, which in turn maximizes the productivity of the gas phase reactor.

This is a particular advantage wherein a comonomer having seven or more carbon atoms is used. Since ethylene-1-octene copolymers have greater impact strength and gaugeability than similar mole % comonomer content copolymers of ethylene with 1-hexene or 1-butene, the process of this invention is of particular advantage in the production of an ethylene-1-octene copolymer. Thus, even when a relatively low mole % content of 1-octene is desired in the copolymer product, the ethylene and 1-octene monomers for its production may be supplied to the reaction zone in concentrations based upon the maximum permissible 1-octene concentration, which, by comparison to prior gas phase processes, means a greater concentration of ethylene and a lesser concentration or even no inert diluent gas is needed, and this maximizes the productivity of the reactor. Likewise, where prior gas phase processes were incapable of producing, at economically feasible production rates, a copolymer having a content of 1-octene of greater than about 0.5 mole %, this invention produces copolymers of ethylene having contents of 0.8 mole % octene and greater at economically feasible production rates.

- 26 -

As noted, the particulars of the pressures and temperatures selected for maintenance within the reaction zone of the reactor will dictate the maximum permissible amount of the selected comonomer which may be supplied thereto; this in turn will dictate the amounts of ethylene and/or inert diluent gas that must be supplied to the reaction zone in order to produce with the particular ionic catalyst used a polymer of the desired amount of incorporated comonomer. Typically, the gas phase reaction may be carried out at pressures ranging from about 50 psi (about 344 kPa) to about 500 psi (about 3500 kPa); and preferably from about 200 psi (about 1379 kPa) to about 350 psi (about 2100 kPa). With respect to the partial pressure selected for the reaction, the amount of catalyst to be supplied is that amount which will maintain a rate of reaction of monomers within the zone sufficient for the cooling system to remove the heat of reaction that will maintain the desired gas temperature within the reaction zone.

#### Copolymer Products of the Method

The copolymers produced by this invention are higher in comonomer content resulting in products of lower density and have higher molecular weight than conventional copolymers. The higher comonomer content of these polymers gives higher tear strength, and allow thinner films to be produced with equivalent tear strengths to films formed from conventional polymers. The copolymers of this invention also produce films of greater clarity.

The copolymer of this invention can be formed into articles, films, adhesives, lubricants, molded articles, melt blown articles, fibers, fabrics, sheets, spun bond fibers or spun bond fabrics by methods well known in the art.

#### EXAMPLES

All Molecular weight are weight average molecular weight unless otherwise noted. Molecular weights ( $M_w$  and  $M_n$ ) were measured by standard Gel Permeation Chromatography techniques known in the art. Melt Index (MI) was measured according to ASTM-D 1238, condition E. Density was measured according to ASTM D -1501. Comonomer content was measured by proton NMR using standard techniques known in the art. Melt Index Ratio is the ratio of  $I_{21}$  over  $I_2$ .  $I_{21}$  is measured by ASTM-D1238-F.  $I_2$  is measured by ASTM-D 1238-E (and is also known as Melt Index). Melt index is inversely proportional to Molecular weight and Melt Index Ratio is directly proportional to molecular weight. Bulk density was measured by the following method: The resin is poured via a 7/8" diameter funnel into a fixed volume cylinder of 400 cc. The bulk density is measured as the weight of the resin divided by 400 cc to give values in g/cc.

- 27 -

Particle size was measured by determining the weight of the material collected in a series of U.S. Standard sieves and determining the weight average particle size based on the sieve series used.

Catalyst system may be produced using the following procedure. First, a silica support is dehydrated at 200°C for 4 hours in a fluidized bed dehydrator. We used Davison 948 silica manufactured by the Davison Chemical Division of W. R. Grace Corporation. Those skilled in the art will appreciate that other supports could be substituted. 800 grams of this dehydrated silica is placed in a clean, dry, nitrogen sparged mixer reactor at 24°C. To this, 2.00 liters of toluene and 1.06 liter of 30% MAO in toluene are rapidly added while stirring. The temperature of the reactor is increased to 68°C and held at this temperature for four hours while continuing mixing. Next, 23 grams of bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride dissolved in .50 liters of toluene are rapidly added while continuing to stir. Synthesis and purification of this metallocene is performed using techniques known to those skilled in the art. The mixer is maintained at 68°C for one hour following the addition of the metallocene. Vacuum is maintained on the reactor until the slurry dries to a free flowing solid with volatiles of 10% or less. Mixing is continued throughout drying. This process yields about 1.0 kg of the completed catalyst system. Those skilled in the art will appreciate that the process can be scaled up to produce the catalyst system in commercial quantities.

In an alternative embodiment, a similar catalyst system is produced using the same bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride metallocene. In this method, however, the MAO is formed in situ. 4.82 liters of a 15% trimethyl aluminum in heptane solution is added to a clean, dry, nitrogen sparged mixer. The reactor is cooled to -4°C. To this solution 700g of hydrated silica with a loss on ignition (OH content) value of 12.5% is slowly added, maintaining a temperature within the range of -4°C to 10°C. The silica addition should occur at a continuous slow rate over a 1 to 2 hour period. Those skilled in the art will appreciate that the reaction of trimethyl aluminum with the moisture contained in the silica is highly exothermic and must be carefully controlled to avoid temperature transients and other process problems. The silica used is Davison 948 manufactured by the Davison Chemical Division of W. R. Grace Corporation. Following completion of silica addition, the temperature is maintained at 10°C and 15.75g of the metallocene dissolved in heptane is added. The reactor temperature is then increased to 68°C over 1 hour, and then is

- 28 -

maintained at 68°C for one hour while mixing. Mixing is then ceased and the solids are permitted to settle for 30 minutes as the temperature is dropped to 38°C. The liquid phase is decanted and the remaining slurry is dried at 68°C under vacuum for about 4 hours, until the residue becomes a free-flowing solid with a volatiles level of 10% or less. This process yields about 0.9 kg of the completed catalyst system.

As described above, bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride supported on silica with a MAO activator produced in accordance with one of the methods described above is a preferred catalyst system and yields good results. However, those skilled in the art will appreciate that a suitable silica supported catalyst system employing this metallocene and an MAO co-catalyst can be produced in a variety of other manners. For example, the absolute and relative amounts of the metallocene and co-catalyst can be varied as necessary to optimize the catalyst system. The support can also be altered.

Further, we have found that other metallocenes can be substituted for that described above. For example, we have achieved generally satisfactory results with other metallocenes, such as bis(n-butyl-cyclopentadienyl) zirconium dichloride and bis(i-propyl-cyclopentadienyl) zirconium dichloride. Each different metallocene will yield a unique composition distribution. As with the preferred metallocene, we have found that these alternatives, when used in supported form in a continuous gas-phase polymerization process, yield resins with a somewhat broader composition distribution and a somewhat higher  $M_z/M_w$  than is obtained when using the same metallocene in its unsupported form. This is very significant because the slight broadening of the composition distribution and the slight increase in  $M_z/M_w$  yield improvements in processability of the resins and also in certain important properties of products incorporating the resins. While we have only tested a relatively small number of metallocenes in the process of this invention, we contemplate that a significant number, including substituted and unsubstituted mono-, bis and tris cyclopentadienyl metallocenes, could be successfully employed. Similarly, it is contemplated that co-catalysts other than MAO could be used. It will also be desirable to use mixed metallocene catalyst systems in some applications. Using a mixed metallocene system will typically yield a broader molecular weight distribution than a single metallocene system.

In the preferred embodiment, the resin is produced using a continuous gas-phase fluidized - bed polymerization process. Such continuous, gas-phase, fluidized bed polymerization processes are well known to those skilled in the art.

- 29 -

Certain parameters of the gas-phase process must be adjusted somewhat where a supported metallocene is used. For example, the rate of comonomer incorporation by a metallocene catalyst is higher than that for a conventional coordination catalyst. Accordingly, to achieve a given density the comonomer should be maintained at a lower concentration in the reactor than would be the case were a Ziegler-Natta catalyst employed. While, we used an 18" (41 cm) gas phase pilot plant, those skilled in the art will appreciate that for other reactor configurations certain of these conditions will vary.

### EXAMPLE 1

#### Catalyst Preparation

To a clean, dry mixer under a blanket of nitrogen were added 800 grams of silica dehydrated at 200 °C with an LOI (loss on ignition) water content of approximately 3 weight percent. To this was added 2000 ml of toluene to suspend the silica. To this, 2.00 liters of toluene and 1.06 liter of 30% MAO in toluene were rapidly added while stirring. The jacket temperature was increased to produce an internal temperature of 155°F (68°C). The temperature was held for four hours with continuous mixing. Next, 23 grams of bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride dissolved in .50 liters of toluene was rapidly added while continuing to stir. This was allowed to react at 155 °F (68°C) for another hour with mixing. The catalyst solids were dried with nitrogen under vacuum at 155°F (68°C) until the catalyst was dry and free flowing. The catalyst had a volatiles content of 10 weight percent or less.

#### Polymerization

An eighteen inch continuous gas phase fluidized bed reactor having a bed of ethylene/ 1-octene granules was used. The gaseous feed streams of ethylene, hydrogen and liquid octene were mixed together in a mixing tee arrangement and introduced below the reactor bed into the recycle gas line. Tri-ethylaluminum (TEAL) was also mixed with this stream as a 1% by weight solution in isopentane carrier solvent. The individual flow rates of ethylene, hydrogen and octene were controlled too maintain fixed composition targets. The ethylene concentration was controlled to maintain a constant ethylene partial pressure of 157 psia (1083 kPa). Equivalently the ethylene concentration was controlled at 50 mole percent. The hydrogen was controlled to maintain a constant hydrogen to ethylene mole ratio. Octene flow rates were controlled at a fixed flow ratio to ethylene. The concentration of octene was also measured by an off-line gas chromatograph to ensure relatively constant octene composition in the recycle gas stream. The 1-



- 30 -

octene was purified before use by purging with nitrogen and treatment in a fixed bed of molecular sieves. The solid catalyst (bis (1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride activated with methyl alumoxane) was injected directly into the fluidized bed using purified nitrogen as the carrier. Its rate was adjusted to maintain a constant production rate. The reacting bed of growing polymer particles was maintained in a fluidized state by continuous flow of the make up feed and recycle gas through the reaction zone. A superficial gas velocity of 1.7 ft/sec was used to achieve this. The reactor was operated at a total pressure of 300 psig (2069 kPa). To maintain constant reactor temperature, the temperature of the recycle gas was continuously adjusted up or down to accommodate any changes in the rate of heat generation due to the polymerization. The fluidized bed was maintained at a constant height by withdrawing a portion of the bed at a rate equal to the formation of particulate product. The product was removed semi-continuously via a series of valves into a fixed volume chamber, which was simultaneously vented back to the reactor. This provided for highly efficient removal of the product, while at the same time recycling a large portion of the unreacted gases back to the reactor. The product, an ethylene-octene copolymer, was then purged to remove entrained hydrocarbons and treated with a small stream of humidified nitrogen to deactivate any trace quantities of residual catalyst. Other parameters and data are summarized in the table below.



- 31 -

Reactor Properties	
Melt Index (dg/min)	1.05
Density (g/cc)	0.9180
Melt Index Ratio	18.1
Physical Properties	
Bulk Density (lb/ft <sup>3</sup> // kg/m <sup>3</sup> )	29.1 / 466.2
Avg. Particle Size (inch / cm)	0.0308 / .078
Fines (%) through 120 mesh	0.58
Ash (ppm)	186
Reactor Concentrations	
Ethylene (mole %)	50.2
Octene (mole %)	0.452
Hydrogen (mole%)	101
Nitrogen (mole%)	47.8
Octene/ethylene mole ratio	0.0090
Hydrogen/ethylene mole ratio	0.00020
TEAL (wt. ppm)	78
Reactor Conditions	
Production Rate (lb/hr // kg/hr)	57.0 // 25.86
Reactor Temp (°F/ °C)	174.1 / 78.94
Catalyst Prod. (lb/lb)	3630
Bed Weight (lb/ kg)	237 / 107.5
Reactor Res. Time (hr)	4.1
Gas Velocity (ft/sec // m/sec)	1.7 // 0.518
Pressure (psig / kPa)	300/ 2068.5

TABLE 1

A'	Cp, Cp* CpR or (C <sub>5</sub> H <sub>5-y</sub> -xS <sub>y</sub> )	(JS', z)	X <sub>1</sub> or X <sub>2</sub>	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium
diethylsilyl	methylcyclopentadienyl	phenylamido	methyl	hafnium
di-n-propylsilyl	1,2-dimethylcyclopentadienyl	p-n-butylphenylamido	ethyl	titanium
diisopropylsilyl	1,3-dimethylcyclopentadienyl	cyclohexylamido	phenyl	Group 5 TM
di-n-butylsilyl	indenyl	perfluorophenylamido	n-propyl	Group 6 TM
di-t-butylsilyl	1,2-diethylcyclopentadienyl	n-butylamido	isopropyl	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl	L or L'
methylphenylsilyl	ethylcyclopentadienyl	ethylamido	amyl	ethylene
ethylmethylsilyl	n-butylcyclopentadienyl	n-propylamido	isoamyl	propylene
diphenylsilyl	cyclohexylmethylcyclopentadienyl	isopropylamido	hexyl	1-butene
di(p-t-butylphenethylsilyl)	n-octylcyclopentadienyl	benzylamido	isobutyl	1,4-hexadiene
n-hexylmethylsilyl	beta-phenylpropylcyclopentadienyl	t-butylphosphido	heptyl	1,3-butadiene
cyclopentamethylenesilyl	tetrahydroindenyl	ethylphosphido	octyl	1,3-hexadiene
cyclo-tetramethylenesilyl	propylcyclopentadienyl	phenylphosphido	nonyl	acetylene
cyclo-trimethylenesilyl	t-butylcyclopentadienyl	cyclohexylphosphido	decyl	methyl-acetylene
dimethylgermyl	benzylcyclopentadienyl	oxo	cetyl	acetylene
diethylgermyl	diphenylmethylcyclopentadienyl	sulfido	methylidene (both X)	ethylacetylene
phenylamido	trimethylgermylcyclopentadienyl		ethylidene (both X)	benzyl
t-butylamido	trimethylstannylcyclopentadienyl	JS' (z-1-y)	ethylidene (both X)	L'
methylamido	triethylplumbylcyclopentadienyl	methoxide		diethylether
t-butylphosphido	trifluoromethylcyclopentadienyl	ethoxide		demethylether
ethylphosphido	trimethylsilylcyclopentadienyl	methylthio		trimethylamine
phenylphosphido	pentamethylcyclopentadienyl (when y = 0)	ethylthio		triethylamine
methylene	fluorenyl			triethylamine
dimethylmethylene	octahydrofluorenyl			triphenyl-phosphine
diethylmethylene	N,N-dimethylamidocyclopentadienyl			tetra-hydrofuran
ethylene	dimethylphosphidocyclopentadienyl			thiophene
dimethylethylene	methoxycyclopentadienyl			dimethyl-sulfide

TABLE 1 (CONT'D)

A'	Cp, Cp* CpR or (C <sub>5</sub> H <sub>5</sub> -y-x-S <sub>x</sub> ) (N,N-dimethylamidomethyl)cyclopentadienyl
dipropylethylene	
propylene	
dimethylpropylene	
diethylpropylene	
1,1-dimethyl-3,3- dimethylpropylene	
tetramethyldisiloxane	
1,1,4,4- tetramethyldisilylethylene	

CLAIMS

## We Claim:

1. A process for preparing a copolymer of ethylene, comprising:  
 continuously contacting a gas mixture comprising ethylene and an  
 olefin comonomer having 7 to 10 carbon atoms present at an ethylene to  
 comonomer molar ratio of up to about 0.2, and wherein the ethylene is present at a  
 partial pressure of about 275 kPa or above and the comonomer is present at a  
 partial pressure of about 13 kPa to about 35 kPa  
 with a catalyst system which comprises:

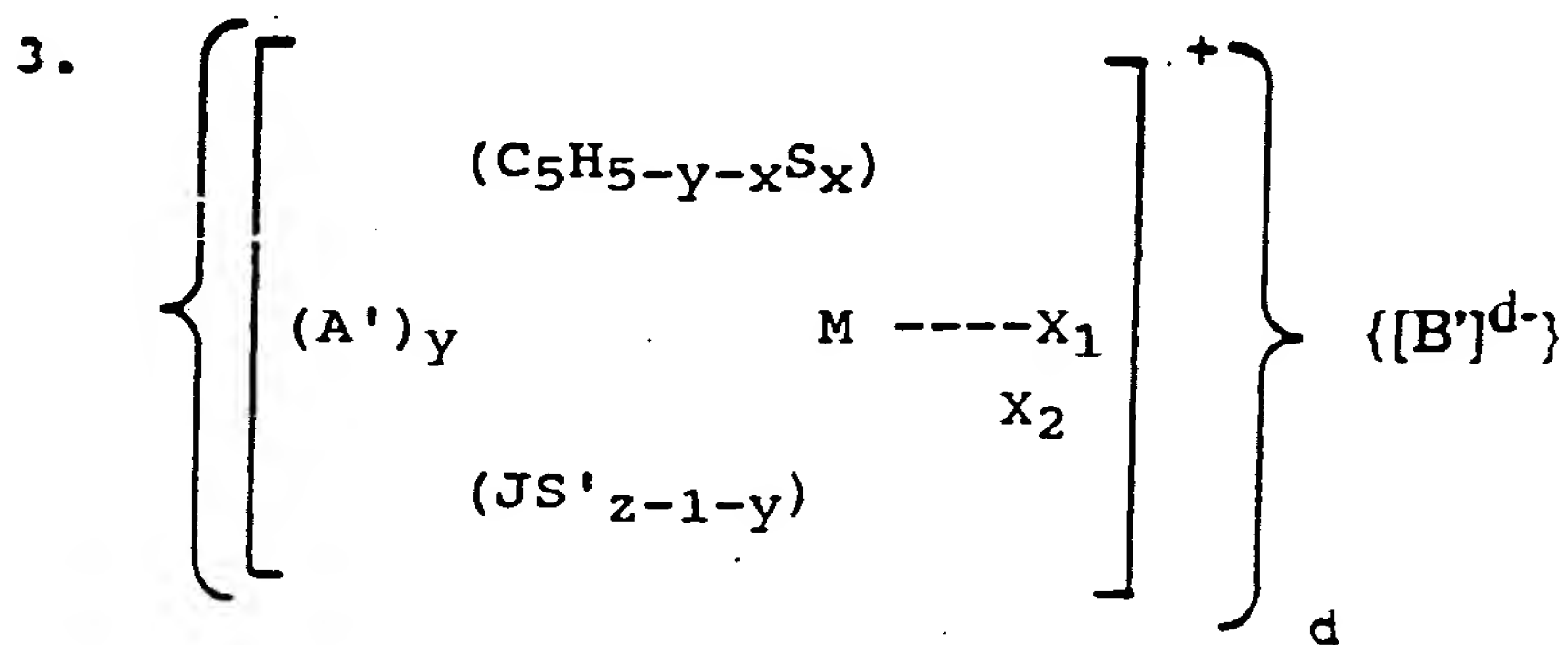
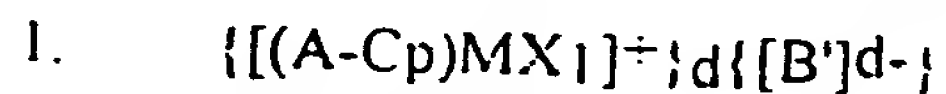
(i) a Group 4, 5 or 6 transition metal compound activated by  
 an alumoxane reagent or

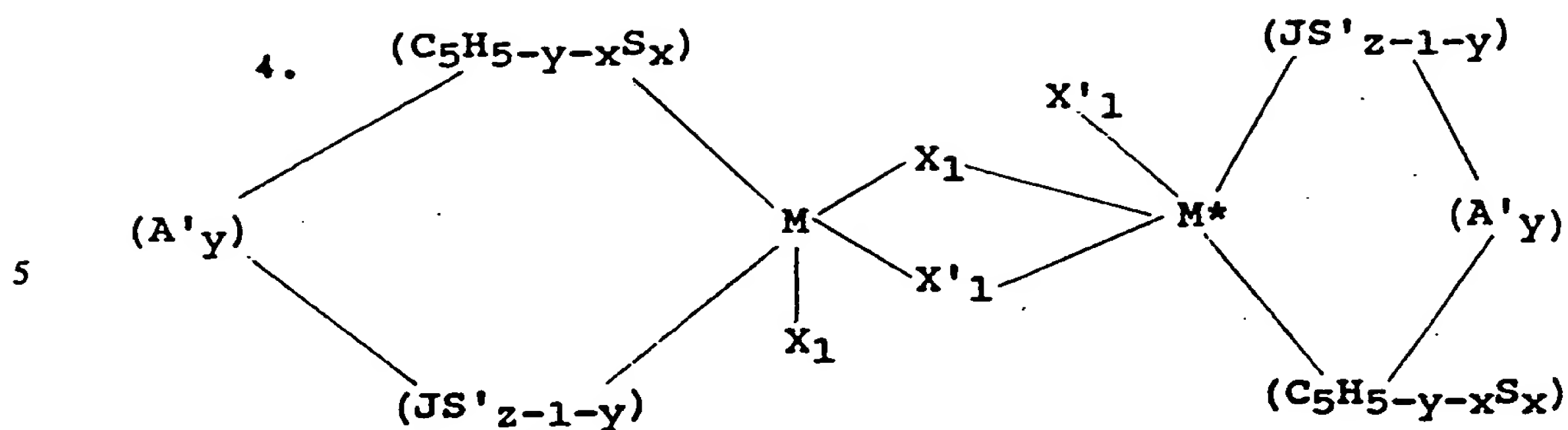
(ii) an ionic product resulting from reaction of a transition  
 metal compound having a hydrolyzable ligand with an activator compound which is  
 reactable with the hydrolyzable ligand to transform the transition metal compound  
 to a cationic transition metal species which is stabilized by a non-nucleophilic anion  
 provided by the reaction of the activator compound.

under gas phase polymerization conditions at a reactor  
 temperature of 60 °C or above.

2. The process of claim 1 further comprising recovering an ethylene  
 copolymer having a molecular weight distribution of 3 or less and a density of  
 about 0.85 to 0.92 g/cc.

3. The process of claim 1, wherein the ionic product comprising the  
 catalyst system is of the following general formulae:





w is an integer from 0 to 3;

10 B' is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms; and d is an integer representing the charge of B'.

15 4. The process of claim 1 wherein the ethylene partial pressure is 689 kPa to 1724 kPa.

5. The process of claim 1, wherein the comonomer is 1-octene.

20 6. The process of claim 2, wherein the ethylene copolymer has a comonomer content of at least 0.8 mole %.

7. The process of claim 1 wherein the polymerization is run at 75°C or above.

25 8. The process of claim 1 wherein the polymerization is run at 60°C to 100°C or above.

9. The process of claim 1 wherein the ethylene to comonomer molar ratio is 0.005 to 0.020.

30 10. The process of claim 1 wherein the comonomer is decene.

11. The process or claim 1 wherein the comonomer is a diene.

35 12. The process of claim 1 wherein the comonomer is norbornene, norbornadiene, 1,7-octadiene, or 1,9-decadiene.

wherein:

(A-Cp) is either (Cp) (Cp\*) or Cp-A'-Cp\*; Cp and Cp\* are the same or different cyclopentadienyl ring substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radical, or Cp and Cp\* are cyclopentadienyl rings in which two adjacent S groups are joined forming a C4 to C20 ring to form a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group which restricts rotation of the Cp and Cp\* rings or (C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) and (JS'<sup>z</sup>-l-y) groups;

(C<sub>5</sub>H<sub>5</sub>-y-xS<sub>x</sub>) is a cyclopentadienyl ring substituted with from zero to five S radicals:

x is from 1 to 0 denoting the degree of substitution;

M is Group 4, 5 or 6 transition metal;

X<sub>1</sub> is hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L' or all or any M, S or S';

(JS'<sup>z</sup>-l-y) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid;

z is the coordination number of the element J;

y is 0 or 1;

L' is an olefin, diolefin or aryne ligand, a neutral Lewis base or a second transition metal compound of the same type such that the two metal centers M and M\* are bridged by X<sub>1</sub> and X'<sub>1</sub>, wherein M\* has the same meaning as M and X'<sub>1</sub> has the same meaning as X<sub>1</sub>; are represented by the formula:



- 36 -

13. The process of claim 1 wherein the alumoxane is methylalumoxane.

14. The process of claim 1, wherein M is a zirconium, titanium or hafnium.

5

15. The process of claim 1, wherein the activator compound is N, N' dimethyl analinium perfluorotetraphenyl boron.

10

16. A process for preparing a copolymer of ethylene and octene, comprising:

15

contacting a gas mixture comprising ethylene and octene in a molar ratio of 0.005 to 0.020 and wherein the ethylene is present at a partial pressure of 275 kPa or above and the octene is present at a partial pressure of 13 to 35 kPa in a gas phase polymerization reaction zone at temperature of 60 °C to 100°C, with a catalyst system which comprises:

(i) a Group 5 or 6 transition metal compound activated by an alumoxane reagent or

20

(ii) an ionic product resulting from reaction of a transition metal compound having a hydrolyzable ligand with an activator compound which is reactable with the hydrolyzable ligand to transform the transition metal compound to a cationic transition metal species which is stabilized by a non-nucleophilic anion provided by the reaction of the activator compound, and recovering an ethylene/octene copolymer having a molecular weight distribution of 3 or less and a density of about 0.85 to 0.92 g/cc.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/07358

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C08F210/16 C08F2/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 323 716 (EXXON) 12 July 1982 see claims see page 3, line 49 - line 56 ---	1
A	EP,A,0 495 375 (THE DOW CHEM COMP) 22 July 1992 see claims see example 2 see page 6, line 39 - line 53 ---	1
A	EP,A,0 452 920 (MITSUI) 23 October 1991 see the whole document -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

5 November 1993

Date of mailing of the international search report

11. 11. 93

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

DE ROECK, R

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/07358

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0323716	12-07-89	US-A- 4814310	21-03-89
		AU-A- 2596188	29-06-89
		DE-A- 3874310	08-10-92
		JP-A- 1207303	21-08-89
		US-A- 4912075	27-03-90
		US-A- 4937217	26-06-90
		US-A- 4925821	15-05-90
		US-A- 4937301	26-06-90
EP-A-0495375	22-07-92	US-A- 5189192	23-02-93
		AU-A- 1023392	23-07-92
		JP-A- 5086120	06-04-93
EP-A-0452920	23-10-91	AU-B- 640559	26-08-93
		AU-A- 1286692	21-05-92
		AU-A- 4011893	26-08-93
		AU-B- 624289	04-06-92
		AU-A- 7502991	24-10-91
		CN-A- 1055935	06-11-91
		JP-A- 4213305	04-08-92
		JP-A- 4213309	04-08-92
		JP-A- 4213306	04-08-92